

(54) ADHERING GLASS AND PLASTIC LENS COMPONENTS
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 (74) CO
 (56) US 4268134
 59010/73 470152 C03C 27/12
 (57) Claim

1. A method of preparing a laminate of glass and a transparent resin with an adhesive thermoplastic polyurethane resin therebetween comprising bringing one surface of the adhesive thermoplastic resin into contact with the glass sheet and the opposite surface of the adhesive thermoplastic polyurethane resin into contact with the transparent resin under conditions to effect lamination thereof, characterised by the lamination being carried out with a solid transparent resin and the polyurethane resin being applied to the glass sheet as a preformed thermoplastic solid, and wherein the polyurethane is a polyester polyurethane that is the reaction product of:

(1) an essentially linear, hydroxy-terminated polyester selected from the group consisting of:

.../2

Patents Act 1953-1959

COMPLETE SPECIFICATION

(ORIGINAL)

54400

FOR OFFICE USE:

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Related Art:

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Detailed Specification for the invention entitled:

**"LAMINATED PHOTOCROMIC LENS AND METHOD OF
LAMINATING A PHOTOCROMIC LENS"**

The following statement is a full description of this invention, including the best method of performing

By way of contrast poly(diethylene glycol bis(allyl carbonate)), a transparent thermoset resin useful for plastic ^{ophthalmic} lenses, has a coefficient of thermal expansion of about 100×10^{-6} per degree centigrade.

This order of magnitude difference can cause stress during fabrication and use which may induce fracture of the glass layer, and delamination of the glass and the surface layer. The delamination is particularly severe during manufacturing processes in which temperatures as high as 150°C may be encountered.

Gulati et al proposes a structure with a ratio of thickness of the plastic front surface layer to the thickness of the plastic back surface layers in the range of about 1 to 8 to about 8 to 1 at all peripheral portions of the lens within about 2 lens thicknesses of the edge, and the adhesive bonding layer is an adhesive having a tensile strength of at least 4000 psi, a shear strength of at least 2000 psi, and an elastic modulus less than 10,000 psi. Exemplary adhesive laminates disclosed by Gulati et al include polyurethanes either formed in situ, or deposited or applied from solution.

Gulati's production technique requires either in situ formation of the adhesive bonding layer on the glass sheet or deposition of the adhesive bonding layer from liquid solution onto the glass sheet, followed by simultaneous in situ polymerization of both transparent thermoset resin layers, i.e., both diethylene glycol bis(allyl carbonate) layers, carried out in contact with both adhesive bonding layers and, further requiring careful control of the temperature profile whereby to avoid bending stresses and meridional stresses during cure. The cure of diethylene glycol bis(allyl carbonate) is characterized by approximately 11 to 14 percent shrinkage of the polymerizing diethylene glycol bis(allyl carbonate).

where the thermoplastic adhesive, e.g., the preformed, solid polyurethane thin sheet, film, or layer, has a combination of elastic properties, e.g., shear strength, tensile strength, elastic modulus, or coefficient of thermal expansion which avoid thermally induced delamination.

5. Detailed Description Of The Invention

As herein contemplated, a glass laminate, such as a glass-plastic laminated lens, is provided. The laminate has a thin, transparent, organic polymeric layer, a thin glass core, and a thin thermoplastic adhesive therebetween. In one exemplification the glass core is a photochromic

10. glass core. The polymeric surface layer may be characterized as a pre-formed thermoplastic resin, as a polyacrylate, a polycarbonate, or a polyvinyl halide, or a preformed thermoset resin, e.g., containing polymerized diol bis(allyl carbonate). It is further characterized by its fracture resistant properties during lamination, which fracture resistant properties may be the result of a substantial absence of creep recovery at strains of from about 0.002 to about 0.01, or the presence of dispersed polymers within the thermoset resin, or the presence of copolymers which modify the ultimate properties or thermal properties of the surface layer.

20. The glass-plastic laminate may be a lens. The laminate may comprise a transparent polymeric front layer or element, a photochromic glass core, and a transparent polymeric back surface layer or element, with each transparent polymeric surface layer or element being bonded to the glass core by an adhesive bonding layer. Alternatively, the laminate may comprise a single transparent polymeric surface layer or element and a glass core, with the glass core being bonded to the transparent polymeric surface layer or element by an adhesive bonding layer. The polymeric surface layer may

absorbers whereby to absorb ultraviolet radiation. Moreover, the adhesive bonding layer and the polymer back surface may have aromaticity incorporated therein. Alternatively or additionally, the back surface layer may have either an infrared absorber or an ultraviolet absorber or both incorporated therein.

5.

Where the surface layer and adhesive bonding layer are between the glass core and the incident light, both the front surface layer and the adhesive layer should be substantially transparent to ultraviolet radiation, that is radiation in the range of 300 nanometers to 400 nanometers, whereby to allow ultraviolet actuated photochromic agents incorporated within the glass core to be effective.

10.

The laminates herein contemplated may be prepared by applying a preformed, solid thin adhesive bonding layer to a surface of a glass core and applying the preformed, solid thin surface layer or element to the preformed, solid adhesive bonding layer. The adhesive bonding layer is applied to the glass core or layer as a preformed, solid, thermoplastic, polymeric material. The surface layer element is applied to the adhesive bonding layer as a solid thermoplastic material or a solid viscoelastic material. The solid material of the surface layer may contain diol bis (allyl carbonate), either as the monomer, having a polymer dispersed therein as will be described herein below, or as a B-stage resin, or as a polymerized solid. Alternatively, it may contain a poly(acrylate), a poly (arylate), a polyvinyl(halide), a poly(carbonate), or a transparent poly(amide).

20.

25.

It is possible to effect lamination to only one surface of the glass core, or to both surfaces sequentially, as well as to both surfaces simultaneously, even to spherically curved glass cores, as herein

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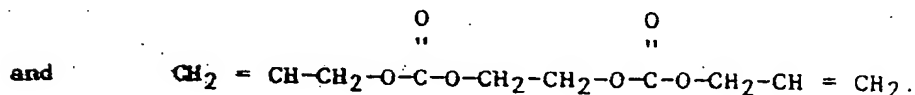
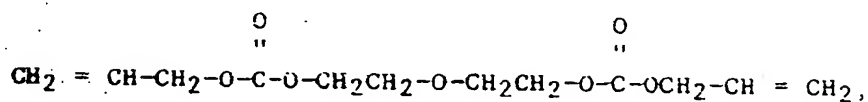
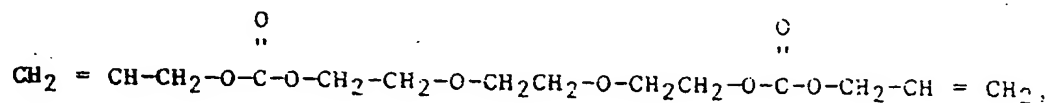
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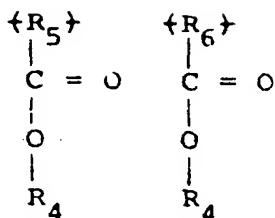
25.

Specific examples of R_2 are alkylene groups such as ethylene, trimethylene, methylethylene, tetramethylene, ethylethylene, pentamethylene, hexamethylene, 2-methylhexamethylene, octamethylene, and decamethylene groups, alkylene ether groups such as $-\text{CH}_2-\text{O}-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$, and $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$, alkylene polyether groups such as $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ groups and alkylene carbonate groups such as $\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2$ and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ groups. Most commonly, R_2 is $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, or $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$.

Specific examples of diol bis(allyl carbonate) monomers useful in the invention herein contemplated include ethylene glycol bis(2-chloroallyl carbonate), diethylene glycol bis(2-methallyl carbonate), triethylene glycol bis(allyl carbonate), propylene glycol bis(2-ethylallyl carbonate), 1,3-propanediol bis(allyl carbonate), 1,3-butanediol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl carbonate), and pentamethylene glycol bis(allyl carbonate).

Commercially important diol bis(allyl carbonate) monomers which are useful in the invention herein contemplated are:

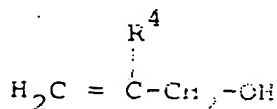




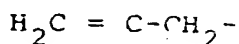
5. where R_5 and R_6 are independently the residues of the acrylic acids $\begin{array}{c} O \\ || \\ R_5-C-OH \end{array}$ and $\begin{array}{c} O \\ || \\ R_6-C-OH \end{array}$ such as acrylic acid,

methacrylic acid, ethyl acrylic acid, butyl acrylic acid, propyl acrylic acid, and higher acrylic acids; and each

10. R_4 is independently hydrogen or the residue of the alcohol R_4OH which is methyl alcohol, ethyl alcohol, an allyl alcohol, or a substituted allyl alcohol, having the formula:

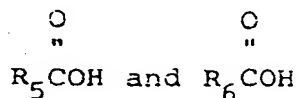


15. where R^4 is chosen from the group consisting of hydrogen, halogen, and C_1 to C_4 alkyls. Most frequently one R_4 is allyl



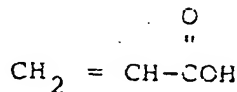
and the other R_4 is hydrogen or ethyl, and

20.

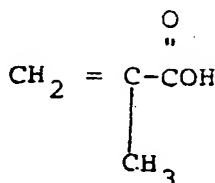


are independently either acrylic acid,

25.



or methacrylic acid



30.

poly(95% methyl methacrylate-5% ^{allyl}allyl methacrylate) of molecular weight approximately 500,000, the system of diethylene glycol bis(allyl carbonate)-poly(95% methyl methacrylate-5% allyl methacrylate), requires partial cure to yield a fabricable resin, while at concentrations above about 10 weight percent poly(95% methyl methacrylate-5% allyl methacrylate) of molecular weight of approximately 500,000, the system of diethylene glycol bis-(allyl carbonate)-poly(95% methyl methacrylate-5% allyl methacrylate) is pseudoplastic upon formation, without cure. At dispersed copolymer concentrations of 5 to 10 weight percent, the system of diethylene glycol bis(allyl carbonate)-poly (95% methyl methacrylate-5% allyl methacrylate) is a thick, syrupy composition approaching thermoplasticity.

The polymer may be added directly to the diol bis(allyl carbonate) monomer. Alternatively, the polymer may be added to an organic solvent, e.g., methylene chloride, whereby to form a solution. Thereafter, the diol bis(allyl carbonate) monomer is added to the solution, and the solvent driven off, e.g., by distillation, evaporation, boiling, or the like.

Especially preferred solvents are those solvents having a solubility parameter of about 9.0 to about 10.0 (calories/cubic centimeter)^{-0.5}, where the solubility parameter is the square root of the cohesive density, as described in F. Rodriguez, Principles of Polymer Systems, McGraw-Hill Book Co., New York, N.Y., (1970), and Beerbower, Kaye, and Pattison, Chem. Engr., December 18, 1967, page 118.

Exemplary solvents include halogenated hydrocarbons, such as methylene chloride, chloroform, dichlorethylene, ethylene dichloride, tetrachloroethane, tetrachloroethylene, trichloroethane, trichloroethylene, aromatics, such as benzene, nitrobenzene, orthodichlorobenzene, styrene, and chlorobenzene, and hydrocarbons. Alternatively, other solvents, such

functionality to provide a copolymerize of a major portion of diol bis(allyl carbonate) and a minor portion of the material having internal polyurethane functionality, i.e., polyurethane material.

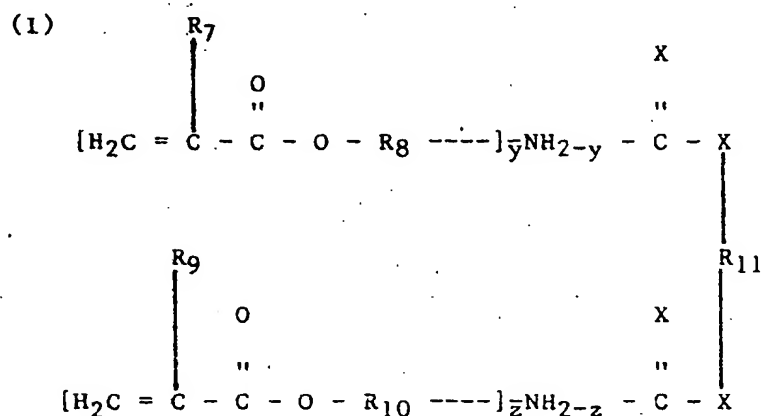
As described in commonly assigned U. S. Patent 4,360,653 of

5. Stevens et al for Polymerizate of (Allyl Carbonate) and Aliphatic Polyurethane Having Acrylic Unsaturation, an effective amount of the acrylated polyurethane material means an amount sufficient to provide a measurable enhancement of impact strength. This is at least about 3 weight percent, and generally above about 10 weight percent. However, the amount should be
10. below about 50 weight percent and preferably below about 40 weight percent in order to retain the desired optical properties and chemical resistance of the diol (allyl carbonate). It has been found that a loading of in excess of about 10 weight percent of the terminal acrylate polyurethane provides a significant increase in average impact strength relative to that of the diol (allyl carbonate) homopolymerizate, while loadings of polyurethane with terminal acrylate functionality above about 20 to 30 weight percent provide an even higher increase in the impact strength relative to that of the polyol(allyl carbonate) homopolymerizate while retaining optical transparency and clarity.

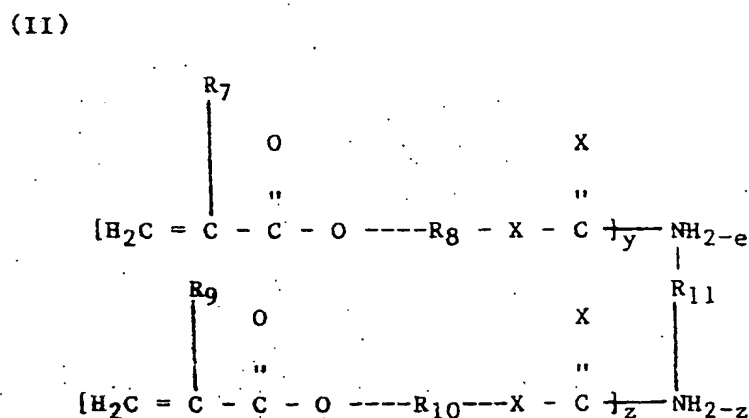
20. However, amounts of the acrylate terminated polyurethane above about 40 to 50 weight percent should be avoided inasmuch as at levels of the acrylate terminated polyurethane above about 40 to 50 weight percent, basis total organics, the chemical resistance of the polymerizate begins to decline relative to that of the diol (allyl carbonate). Nevertheless, higher levels of acrylate terminated polyurethane may be utilized where chemical resistance is not essential.

The polyurethanes having terminal acrylate functionality which can be copolymerized with the diol bis(allyl carbonate) to yield the rigid outer surface or lens according to this invention are normally liquid, aliphatic diacrylate, triacrylate, and ^{tetraacrylate} ~~tetraacrylate~~ polyurethanes.

5. According to one exemplification herein contemplated, the polyacrylate having internal polyurethane, including dithiocarbamate, functionality has the formula:



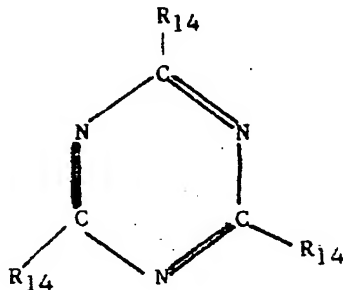
while according to an alternative exemplification, the polyacrylate having internal polyurethane functionality has the formula:



i.e.,

According to a further embodiment of the exemplification where the diol bis(allyl carbonate) is copolymerized to enhance the elastic properties, ultimate properties, or thermal properties, the copolymer may be an allyl S-triazine.

5. Allyl S-triazine has the formula:



10. where the R_{14} 's are independently chosen from the group consisting of -H, and $-OCH_2CH=CH_2$ with at least one R_{14} being an ^{allyloxy}~~allyl~~ group. Most commonly the R_{14} 's are $-OCH_2CH=CH_2$, and the trifunctional monomer triallyl cyanurate is copolymerized with the diol bis(allyl carbonate).

15. The surface layers, e.g., the spherically curved, transparent, polymeric layers, herein contemplated may be prepared by adding an effective amount of an allyl S-triazine, e.g., triallyl cyanurate to a diol bis(allyl carbonate) monomer whereby to provide a liquid composition of an effective amount of the allyl S-triazine and the balance diol bis(allyl carbonate), i.e., a minor portion of allyl S-triazine and a major portion diol bis(allyl carbonate).

20. By an effective amount of allyl S-triazine is meant an amount sufficient to provide a measurable enhancement of impact strength or heat distortion temperature of the copolymer of allyl S-triazine and diol bis(allyl carbonate), i.e., at least about 2 weight percent in the case of triallyl cyanurate. However, preferably the amount of allyl S-triazine should be below 40 weight percent whereby to retain the desirable optical properties of the diol bis(allyl carbonate).

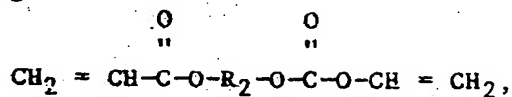
or their anhydrides, such as maleic and fumaric acids, and the alkyl, e.g., methyl, ethyl, or halogenated, e.g., chloro-, bromo- derivatives thereof. Mixtures of the aforementioned unsaturated acids and of the acids and anhydrides can, of course, be used in the preparation of the unsaturated polyester.

Polyhydric alcohols e.g., glycols, that can be used to produce the above-described unsaturated polyesters are aliphatic alcohols containing two or more hydroxy groups. Typical of the polyhydric alcohols used to prepare unsaturated polyester resins are glycols containing from 2 to about 10 carbon atoms such as the polymethylene glycols in the series from ethylene glycol to decamethylene glycol. Also included are the branched alcohols such as are present in the propylene and butylene glycols. Preferably, the glycols contain from 2 to 6 carbon atoms and will be hydroxy terminated. Also useful are the polyethylene glycols in the series from diethylene glycols to triethylene glycol, and the polypropylene glycols, e.g., dipropylene glycol and tripropylene glycol. Particularly useful are diethylene and triethylene glycol. Most preferred are glycols containing from 2 to 4 carbon atoms, i.e., ethylene glycol, 1-3-propylene glycol, and 1,4-butane diol.

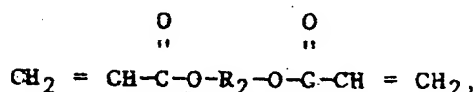
The preferred polymerizable unsaturated polyesters used in the polymerizable liquid compositions are the so-called "linear polyesters," i.e., those which have little cross-linking in the polyester molecules, as evidenced by the fact that such polyesters are soluble in solvents such as acetone.

Suitable unsaturated monomers include liquid lower alkyl esters of unsaturated carboxylic acids, vinyl esters of the lower members of saturated monocarboxylic acids, and styrene.

where R_2 is as defined above, an analogous poly(acrylyl carbonate) polymerizate, e.g.:

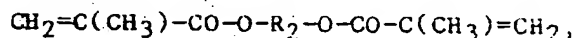
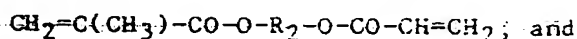
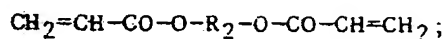


5. where R_2 is as defined above, or an analogous poly(acrylate) polymerizate, e.g.:



as described herebelow, where R_2 is as defined herein, and interpolymers
10. of two or more of allyl carbonates, vinyl carbonates, acrylyl carbonates, and acrylates.

Acrylate monomers which may be utilized in this invention to provide the transparent, polymeric surface element include acrylic acids, e.g., acrylic acid, $\text{CH}_2=\text{CH}-\text{CO}-\text{OH}$, and methacrylic acid, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{OH}$;
15. acrylate esters, e.g., ethyl acrylate, $\text{CH}_2=\text{CH}-\text{CO}-\text{OCH}_2\text{CH}_3$, and methyl methacrylate, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{OCH}_3$. Alternatively, multifunctional acrylates may be utilized in this invention, e.g.,



where R_2 is chosen from the group consisting of aryl groups and alkylene groups such as ethylene, trimethylene, methylenemethylene, tetramethylene, ethylethylene, pentamethylene, hexamethylene, 2-methylhexanethylene, octamethylene, and ~~decamethylene~~ ^{decamethylene} groups, alkylene ether groups such as

25. $-\text{CH}_2-\text{O}-\text{CH}_2-$, $-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$

groups, alkylene polyether groups, such as $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ and

$-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ groups, and alkylene carbonate groups,

such as $-\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2-$.

Most commonly R_2 for diacrylates is $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}_2-$

30. $-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$.

According to the invention herein contemplated the thermal properties of the adhesive bonding layer, including the thermal dependencies of the ultimate properties, provide low temperature pliability so that the laminate is resistant to thermal shock, e.g. when going from temperatures below about 0°C or even below about -17°C to temperatures above about 25°C or even above 100°C. Additionally, the thermal properties, including the thermal dependencies of the ultimate properties, are believed to permit the lamination of precast transparent outer elements to glass with the precast solid adhesive bonding layer herein contemplated. In this way the use of adhesive solutions in the lamination process is avoided.

Additionally, for optical and ^{ophthalmic} ~~ophthalmic~~ applications, the adhesive bonding layer should have optical clarity, low haze, maximum light transmission, and sufficient ultraviolet transmission to allow the photochromic agent, if any, in the glass core, to function effectively. The adhesive bonding layer is above about 0.002 inch thick, and preferably from about 0.005 inch thick to about 0.02 inch thick.

Exemplary adhesive bonding materials include polyurethanes, polyesterurethanes, polyetherurethanes and polycarbonateurethanes, and poly(vinyl butyral)s. Preferably, the adhesive bonding layer closest to the incident light source, is a polyurethane that is transparent to ultraviolet radiation as defined hereinabove, whereby to allow ultraviolet activation of the photochromic materials within the glass core. For this reason the diisocyanate is an aliphatic diisocyanate compound. Preferred are cycloaliphatic compounds, especially dinuclear compounds bridged by an isopropylidene group or an alkylene group of 1 to 3 carbon atoms. Among the aliphatic diisocyanate that can be used are hexamethylene diisocyanates. Among the cycloaliphatic diisocyanates which can be employed are 4,4'-methylene-bis-(cyclohexyl diisocyanate), hydrogenated toluene diisocyanate.



The preferred urethanes of the invention can be characterized as plastomers, that is, they are elastoplastic and thus do not snap back as a true elastomer when stressed. In addition, they are optically clear when used in laminates in thin sections, e.g., from less than about 10 to 60 mils, flexible and essentially non-adhesive at room temperature. They can also be described as being leathery, thermoplastic polymers that generally have a relatively constant Gehman modulus at between about -20°C. and 50°C. of 1×10^7 and $1 \times 10^{9.5}$. The Gehman modulus is measured according to ASTM-D 1053-65. The Gehman modulus should be taken within a few days or not more than a month after the polyurethane sheet is formed as the Gehman modulus may change upon aging. The preferred laminates are resistant to shock and impact and, when incorporated as part of a laminate, e.g., a ~~glass-thermostat~~ ^{glass-thermoset} resin laminate, impart penetration resistance to the laminate over a wide temperature range. These properties are provided by polyester polyurethanes, polycarbonate polyurethanes and polyether polyurethanes.

Polyester compositions useful in preparing polyesterurethanes that can be used to prepare the above-described laminated articles are hydroxy-terminated polyesters having a number average molecular weight of between about 500 and about 5000, particularly between 750 and 4000 and, more particularly, between 1000 and 3300. More preferably, the polyesters are aliphatic, essentially linear polyesters having a number average molecular weight of between about 1000 and about 3300, which are prepared by esterification of an aliphatic dicarboxylic acid, or anhydride thereof, with an aliphatic polyhydric alcohol, e.g., an aliphatic diol. The number average molecular weight of the polyester compositions useful in the present invention can be determined by hydroxyl end group analysis and by the following formula:

$$\text{No. Ave. Mol. Wt.} = \frac{(\text{functionality of the polyester})(56.1)(1000)}{\text{hydroxyl (OH) number of the polyester}}$$



Examples of polyhydric alcohols of from 2 to 15 carbon atoms inclusive which can be used to form the polyester include: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl propane diol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,10-decanediol, and unsaturated diols such as 2-butene-1,4-diol, 2-butyne-1,4-diol and the like. Mixtures of polyhydric alcohols, e.g., ethylene glycol and propylene glycol, can be employed. Only small amounts, if any, of trifunctional alcohols, such as glycerol or trimethylol propane should be present in order to decrease the possibility of extensive cross-linking since the preferred polyesters are essentially linear. Preferably, no trifunctional alcohols are present.

Examples of preferred polyesters include poly(1,4-butylene adipate), poly(1,4-butylene succinate), poly(1,4-butylene glutarate) poly(1,4-butylene pimelate), poly(1,4-butylene suberate), poly(1,4-butylene azelate), poly(1,4-butylene sebacate), and poly(epsilon caprolactone).

The polyester compositions useful in the present invention can, as indicated, have a number average molecular weight of between about 500 and 5000. It is understood that this is a number average and that the polyester composition is composed of a great number of different molecules of varying length, i.e., from the free glycol to a high molecular weight polyester, in a normal distribution. For example, a poly(1,4-butylene adipate) of 2000 number average molecular weight will have molecular species contained in it ranging from unreacted residual 1,4-butanediol (molecular weight 90) to poly(1,4-butylene adipates) of 5000 molecular weight or higher; but, with the principal constituents of the composition (in weight) being in the near vicinity of 2000 molecular weight to achieve

The simple segmented polyurethanes of the present invention are composed of two segments: (a) a hard segment which is composed of the reaction product of the low molecular weight active hydrogen compound, e g., the aliphatic diol, and the diisocyanate; and (b) a soft segment which is composed of the reaction product of the polyesterdiol or polyetherdiol and the diisocyanate. The hard and soft segments are bonded together through the urethane linkage. Generally, the higher the molecular weight of the polyesterdiol or polyetherdiol, the higher the weight percent hard segment of the polyurethane. The preferred polyurethanes of the present invention and those that are useful for the preparation of penetration (impact) resistant laminates will have a weight percent hard segment of from about 10 to about 45 percent, preferably from 15 to 36 percent. More particularly, when the polyetherdiol or polyesterdiol has an average molecular weight of about 2000, the hard segment of the polyurethane will range preferably from about 15 to about 30 percent. The weight percent hard segment (H.S.) can be calculated from the expression:

$$\text{WT.\%H.S.} = \frac{[(\text{Moles of low molecular weight active hydrogen compound}) \times (\text{Molecular weight of low molecular weight active hydrogen compound} + \text{molecular weight of diisocyanate})] \times 100}{\text{Total Wt. of Reactants}}$$

The preferred polyurethanes of the invention are amorphous and will generally have an average molecular weight, as calculated from inherent viscosity measurements, of between about 10,000 and about 100,000 and preferably between about 20,000 and about 65,000.

Exemplary polyesterurethanes containing from about 25 to about 30 weight percent hard segment have an elastic modulus at -35°C of about 1,500 to about 2,300 pounds per square inch at 100 percent elongation, about 3,500 to 4,500 pounds per square inch at 200 percent elongation, and about 5,400 to about 6,100 pounds per square inch at 300 percent elongation; an

methyl methacrylate, and about 1.0 weight percent benzoyl peroxide dispersed therethrough. The plastic surface layers have a substantial absence of creep recovery at strains of from about 0.002 to 0.01. Cure is effected by a post lamination heating to about 300°F.

5. According to a further exemplification of the invention herein contemplated a three layer laminate lens is produced. The lens has a front surface of a 0.02 inch thick, 3 inch diameter, plus 6.00 base curvature photochromic glass lens, a 0.040 inch thick polymeric diethylene glycol bis(allyl carbonate) plastic back surface layer, and a 0.015 inch thick, three inch diameter polyesterurethane adhesive layer between the glass lens and the plastic lens.

10. In an alternative embodiment of this exemplification the plastic surface layer is a partially cured polymerizate of diethylene glycol bis(allyl carbonate) having about 2 to 7 weight percent of a 300,000 to 500,000 viscosity average molecular weight copolymer of 93 to 97 weight percent methyl methacrylate and 3 to 7 weight percent allyl methacrylate, and 0.5 to 1.5 weight percent benzoyl peroxide dispersed therethrough. After lamination at 270°F. a post cure is carried out at 300°F.

15. According to a still further exemplification a five layer laminated lens is prepared where the plastic surface and the adhesive bonding layer between the photochromic glass core and the incident light are substantially transparent to ultraviolet radiation, but either the back plastic surface or the back adhesive binding layer or both are responsive to ultraviolet radiation. For example, either the adhesive binding layer or the back plastic surface or both may have an ultraviolet radiation absorbing amount of aromaticity. Alternatively, the front plastic surface layer and adhesive binding layer may be dispensed with and the back plastic surface layer and the back adhesive binding layer may be ultraviolet radiation absorbers incorporated therein.

20. The following examples are illustrative of this invention:

Adhesive Bonding Layer

5. The adhesive bonding layer was a polyester polyurethane having a soft segment and a hard segment. The soft segment was the reaction product of poly(1,4-butane diol adipate) having a number average molecular weight of about 2000 and 4,4'-methylene bis(cyclohexyl ^{isocyanate} ~~diisocyanate~~). The hard segment was the reaction product of 1,4 butane diol and 4,4'-methylene ^{bis (cyclohexyl isocyanate)} ~~diisocyanate~~. The weight ratio of hard segment to total hard and soft segment was about 0.25 to 1.

Adhesion Promoter

10. A solution of 0.5 Union Carbide Silane 1100 in methanol was prepared.

Lamination

15. A laminate was prepared by placing a Teflon® polytetrafluoroethylene sheet, a 0.065 inch thick plastic lens, a 0.020 inch thick polyester polyurethane layer, a 0.020 inch thick curved glass lens, a 0.020 inch thick polyester polyurethane layer, a 0.005 inch thick plastic lens, and a Teflon® polytetrafluoroethylene sheet between two plus 6 base curvature lens grinding mandrels, each of the interior surfaces of the plastic lenses, adhesive bonding layer sheets, and glass lens having been wetted with the silane adhesion promoter.
- 20.

The assembly was pressed at 300°F. (149°C) for about 2 to 3 minutes at a pressure of about 200 to 300 pounds per square inch.

The resulting laminated lens had good adhesion.

EXAMPLE II

25. The procedure of Example I was followed with the following changes:

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of preparing a laminate of glass and a transparent resin with an adhesive thermoplastic polyurethane resin therebetween comprising bringing one surface of the adhesive thermoplastic resin into contact with the glass sheet and the opposite surface of the adhesive thermoplastic polyurethane resin into contact with the transparent resin under conditions to effect lamination thereof, characterised by the lamination being carried out with a solid transparent resin and the polyurethane resin being applied to the glass sheet as a preformed thermoplastic solid, and wherein the polyurethane is a polyester polyurethane that is the reaction product of:

(1) an essentially linear, hydroxy-terminated polyester selected from the group consisting of:

- (a) poly(1,4-butylene adipate) having a molecular weight of 1000 to 2000;
- (b) poly(1,4-butylene azelate) having a molecular weight of 1000 to 2000; and
- (c) poly(epsilon caprolactone) having a molecular weight of 1000 to 2000;

(2) an aliphatic diol having from 2 to 10 carbon atoms; and

(3) 4,4'-methylene bis(cyclohexyl isocyanate);

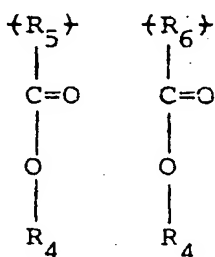
the mole ratio of aliphatic diol to polyester is from 0.7:1 to 5.0:1, the quotient of

$$\left(\text{Moles of Aliphatic Diol} \right) \left[\left(\text{Molecular Weight of Aliphatic Diol} \right) + \left(\text{Molecular Weight of Isocyanate} \right) \right]$$

Total Weight of Reactants

5. diol bis(allyl carbonate) copolymers with an ultimate physical property enhancing copolymer, poly(acrylates), poly(arylates), poly(vinyl halides), poly(carbonates), poly(vinyl carbonates), poly(acrylyl carbonates), and poly(amides).

7. The method of Claim 6 wherein the transparent resin is diol bis(allyl carbonate) having a second polymer dispersed therethrough, the second polymer having the formula:



10. where R_5COOH and R_6COOH are independently chosen from the group consisting of acrylic acid, methacrylic acid, ethyl acrylic acid, butyl acrylic acid, and propyl acrylic acid, and R_4OH is independently chosen from the group consisting of water, methyl alcohol, ethyl alcohol, and allyl alcohol.

8. The method of Claim 7 wherein the second polymer is chosen from the group consisting of poly(methyl methacrylate) and poly(allyl methacrylate-methyl methacrylate).

9. The method of Claim 6 wherein the transparent resin is diol bis(allyl carbonate) having an ultimate physical property enhancing copolymer chosen from the group consisting of allyl S-triazines and acrylate terminated polyurethanes.

(c) poly(epsilon caprolactone) having a number average molecular weight of 1000 to 3300;

25.

(2) an aliphatic diol having from 2 to 10 carbon atoms; and

(3) 4,4'-methylene bis(cyclohexyl isocyanate)

in which the mole ratio of aliphatic diol to polyester is

30.

from 0.7:1 to 5.0:1, the quotient of

$$\frac{\left(\begin{array}{c} \text{Moles of Aliphatic} \\ \text{Diol} \end{array} \right) \left[\begin{array}{c} \text{Molecular Weight of} \\ \text{Aliphatic Diol} \end{array} \right] + \left(\begin{array}{c} \text{Molecular Weight} \\ \text{of Isocyanate} \end{array} \right)}{\text{Total Weight of Reactants}}$$

is from 0.15 to 0.36, the number of isocyanate groups provided

35.

by the 4,4'-methylene bis(cyclohexyl isocyanate) being substantially equivalent to the total number of hydroxy groups provided by the polyester and the aliphatic diol whereby the polyester urethane is substantially free of unreacted

isocyanate groups; and wherein said lens is the product

40.

produced by the process of laminating together said thin glass layer, said adhesive polyurethane resin layer as a preformed solid, and said transparent polymeric surface layer as a preformed solid.

14. The laminated ophthalmic lens of Claim 13 wherein said thin glass layer has a thickness of from 0.01 to 0.050 inch.

15. The laminated ophthalmic lens of Claim 13 wherein said thin glass layer has a thickness of from 0.015 to 0.030 inch.

16. The laminated ophthalmic lens of Claim 13 wherein said adhesive thermoplastic polyurethane resin layer has a thickness of from 0.002 inch.

24. The laminated ophthalmic lens of Claim 13 which is spherically curved.

25. The laminated ophthalmic lens of Claim 13 wherein:

- (a) said adhesive thermoplastic polyurethane resin layer has a thickness of from 0.005 to 0.02 inch;
- (b) said aliphatic diol is 1,4-butane diol;
- (c) said 4,4'-methylene bis(cyclohexyl isocyanate) has a stereoisomer content of 19 to 21 percent trans, trans, 17 to 18 percent cis, cis, and 62 to 64 percent cis, trans; and
- (d) said transparent polymeric surface layer is polymer of diethylene glycol bis(allyl carbonate).

26. The laminated ophthalmic lens of Claim 25 wherein said thin glass layer is photochromic.

27. The laminated ophthalmic lens of Claim 25 which is spherically curved.

28. A laminated ophthalmic lens comprising:

- (a) a thin glass layer having a thickness of from 0.005 to 0.100 inch;
- (b) a first transparent polymeric surface layer comprising polymer of a polyol (allyl carbonate);
- (c) a second transparent polymeric surface layer comprising polymer of a polyol (allyl carbonate);

- provided by the 4,4'-methylene bis(cyclohexyl isocyanate) being substantially equivalent to the total number of hydroxy groups provided by the polyester and the aliphatic diol whereby the polyester urethane is substantially free of unreacted isocyanate groups; and wherein said lens is the product produced by the process of laminating together said thin glass layer, both of said adhesive polyurethane resin layers as preformed solids, and both of said transparent surface layers as preformed solids.
45. 50.

29. The laminated ophthalmic lens of Claim 28 wherein said thin glass layer has a thickness of from 0.01 to 0.050 inch.

30. The laminated ophthalmic lens of Claim 28 wherein said thin glass layer has a thickness of from 0.015 to 0.030 inch.

31. The laminated ophthalmic lens of Claim 26 wherein each of said adhesive thermoplastic polyurethane resin layers has a thickness above 0.002 inch.

32. The laminated ophthalmic lens of Claim 28 wherein each of said adhesive thermoplastic polyurethane resin layers has a thickness from 0.005 to 0.02 inch.

33. The laminated ophthalmic lens of Claim 28 wherein said aliphatic diol is selected from the group consisting of 1,4-butane diol, 1,3-butane diol, and 1,6-hexane diol.

34. The laminated ophthalmic lens of Claim 28 wherein said aliphatic diol is 1,4-butane diol.

- (c) said 4,4'-methylene bis(cyclohexyl isocyanate has a stereoisomer content of 19 to 21 percent trans, trans, 17 to 18 percent cis, cis, and 62 to 64 percent cis, trans; and
- (d) each of said transparent polymeric surface layers is polymer of diethylene glycol bis(allyl carbonate).

41. The laminated ophthalmic lens of Claim 40 wherein said thin glass layer is photochromic.

42. The laminated ophthalmic lens of Claim 40 which is spherically curved.

43. A laminated photochromic lens substantially as hereinbefore described with reference to the examples.

DATED this 27th day of March, 1985.

PPG INDUSTRIES INC.,
By their Patent Attorneys,
COLLISON & CO.

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